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THE PREPARATION OF SPECIFIC ADSORBENTS

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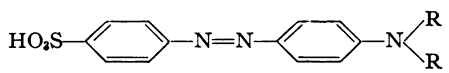
A method has been developed for preparing adsorbents having specific affinities for predetermined substances. This method consists in forming the structure of the adsorbent in the presence of the particular compound for which it is desired to prepare a specific adsorbent. The presumable explanation of the formation of a specifically attracting structure under these conditions is that the adsorbent in the process of formation has accessible to it a very great number of structures which differ only slightly in stability, and that in the presence of a foreign molecule those structures that are stabilized through attraction for the foreign molecule are preferentially assumed. The adsorbent is thus pictured as automatically forming pockets that fit closely enough to the foreign molecule to hold it by van der Waals' forces, hydrogen bonds, interionic attractions, and other types of intermolecular interaction. This mechanism is the same as that proposed by Pauling[1] for the formation of antibodies with use of antigen molecules as a template, which formed the basis for the manufacture of artificial antibodies reported by Pauling and Campbell.[2]

An experimental test of the idea has been made by the formation of silica gel in the presence of methyl orange and some of its homologs—ethyl, *n*-propyl and *n*-butyl orange. These compounds have the following structure:



where *R* represents the radicals named. The adsorbents were prepared by mixing 0.5 g. of finely divided dye with 30 ml. of aqueous sodium silicate (d^{20} 1.401) 275 ml. of water and 30 ml. of glacial acetic acid, drying (at room temperature), grinding and sieving the resultant gels, and subjecting the fraction between 48 and 200 mesh to methanol extraction, which removed most of the dye. Control gels, without dye, were prepared in the same way.

The gels were tested as adsorbents by bringing 1-g. samples into equilibrium with 10-g. portions of standard solutions of the dyes in 5% acetic acid. The initial dye concentrations were 1.5×10^{-5} formal. The final concentrations in the supernatant solutions were measured with a spectrophotometer and the quantity adsorbed was calculated by difference. In order to obtain accurate estimates of the dye concentrations from the spectrophotometer readings it was necessary to correct these readings for the cloudiness which appeared in the solutions after contact with the silica gel samples. Such corrections were calculated on an empirical basis from readings taken in another portion of the spectrum where the dye absorptions are negligible. The ratio of the concentration in the gel to that in the supernatant solution was then calculated as a measure of the "adsorption power" of the gel for the particular dye. The following results were obtained.

TABLE 1

	ADSORPTION POWER FOR:			
	METHYL ORANGE	ETHYL ORANGE	PROPYL ORANGE	BUTYL ORANGE
Control gel	84	80	240	320
Specific adsorbent	300	740	5000	5000

In order to show that this process has effected a specific rather than a general enhancement of the adsorption properties of the gels, adsorption powers were determined with each of the gels for each of the dyes. The ratio of these adsorption powers to the adsorption powers shown for the particular dyes by the control gels were then calculated. These "relative adsorption powers" are tabulated below.

TABLE 2

	RELATIVE ADSORPTION POWER FOR:			
	METHYL ORANGE	ETHYL ORANGE	PROPYL ORANGE	BUTYL ORANGE
Gel prepared with:				
Methyl orange	3.5	1.6	1.1	1.1
Ethyl orange	2.5	9	2.1	2.2
Propyl orange	2.3	5	20	6
Butyl orange	1.5	2.8	5	15

It is difficult to reproduce exactly the adsorption properties of silica gel samples and these data are to be regarded primarily as a qualitative demonstration of the preparation of specific adsorbents. However, the essential features of the above table, maximum adsorption power for the dye used in the preparation of the adsorbent, and sharply decreasing adsorption powers for the dyes of decreasing similarity of molecular structure, have been observed in several independent experiments. Gels prepared with this series of compounds are not better adsorbents than the control gels for a struc-

turally unrelated dye, fluorescein. The results obtained with this series of compounds are especially striking because the dyes differ only in the nature of the alkyl groups. Still more pronounced effects would be expected in studies of compounds having greater structural differences.

Many obvious applications and extensions of these ideas are now being investigated and detailed results will be published later. Of particular interest are an investigation of the possibility that optical isomers can be separated with such adsorbents and an attempt to demonstrate "specific catalysis," analogous to the action of enzymes, by specific adsorbents for the reactants or products of various reactions.

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[1] Pauling, L., *J. Am. Chem. Soc.*, **62**, 2643–2657 (1940).

[2] Pauling, L., and Campbell, D. H., *J. Exptl. Med.*, **76**, 211–220 (1942).

THE VALENCE-STATE ENERGY OF THE BIVALENT OXYGEN ATOM

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A significant simplification in the discussion of the structure of molecules can be achieved by referring the energies of molecules not to the energies of their constituent atoms in any one of the stationary spectroscopic states of the isolated atoms, but instead to a hypothetical valence state of each atom.[1] The valence state of an atom is defined as that state in which it has the same electronic structure as it has in the molecule. Thus in the valence state the spins of the electrons that are used for forming bonds in a molecule are considered to resonate between positive and negative values, corresponding to the resonance of each bonding electron with another electron of opposite spin in the atom with which the bond is formed. For the bivalent oxygen atom, with six L electrons, two orbitals, one mainly $2s$ in character and one $2p$, are occupied by unshared pairs, and the other two orbitals, mainly $2p$ but with a small amount of s hybridization, are occupied by one bonding electron apiece, the spins of which are parallel 50 per cent of the time and antiparallel 50 per cent of the time. In the following paragraphs values of the energy of this bivalent state of the oxygen atom relative to the normal state of the isolated atom, ^3P, are derived by four different methods. It is found that the four values agree